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14. ABSTRACT

Two efficient processes for the synthesis of twelve, relatively water soluble, heterocyclium *closo*-dodecaborane $[B_{12}H_{12}]^{-2}$ and *closo*-dodecacarborane $[CB_{11}H_{12}]^{-1}$ salts by a one-step, open-air metathesis reaction have been developed. First, a combination of exhaustive trituration of the two solid reactant salts with refluxing anhydrous acetonitrile followed by flash filtration through a plug of silica gel affords excellent recovery for a broad series of otherwise water-soluble salts. Second, an alternative aqueous metathesis, driven to completion by precipitation of silver halides, followed by removal of water, re-dissolution in acetonitrile, and filtration through a plug of silica gel, affords complex heterocyclium borane salts albeit with possible minor "bleed-through" of the by-product KNO_3 salt. Mixed cation heterocyclium dodecaborane salts also can synthesized, and one example analyzed, shows melting point depression behavior.

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PAIRING HETEROCYCLIC CATIONS WITH *CLOSO*-ICOSAHEDRAL BORANE AND CARBORANE ANIONS, II: BENCHTOP ALTERNATIVE SYNTHETIC METHODOLOGIES FOR BINARY TRIAZOLIUM AND TETRAZOLIUM SALTS WITH SIGNIFICANT WATER SOLUBILITY

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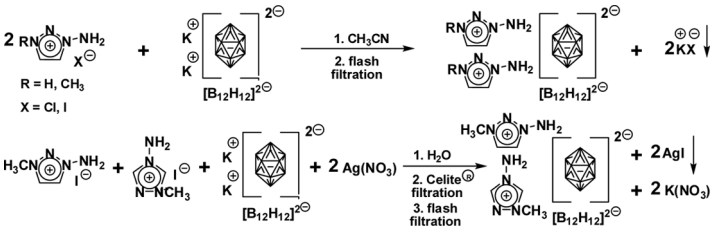
GRAPHICAL ABSTRACT



Abstract *Two efficient processes for the synthesis of 12 relatively water-soluble binary triazolium and the first tetrazolium borane $[B_{12}H_{12}]$ and carborane $[CB_{11}H_{12}]$ salts by a one-step, open-air metathesis reaction have been developed. First, a combination of exhaustive trituration of the two solid reactant salts with refluxing anhydrous acetonitrile followed by flash filtration through a plug of silica gel afforded excellent recovery for a broad series of otherwise water-soluble heterocyclium salts. Second, an alternative aqueous metathesis, driven to completion by precipitation of silver halides, followed by removal of water, redissolution in acetonitrile, and filtration through a silica-gel plug, also yielded such heterocyclium borane and carborane salts. Mixed 1:1 dication heterocyclium borane salts were first synthesized using this second procedure, and one example showed melting-point depression behavior.*

Keywords *closo*-Icosahedral borane dianions; *closo*-icosahedral carborane anions; exhaustive trituration; heterocyclium halides; mixed heterocyclium boranes; silver-halide-mediated metathesis

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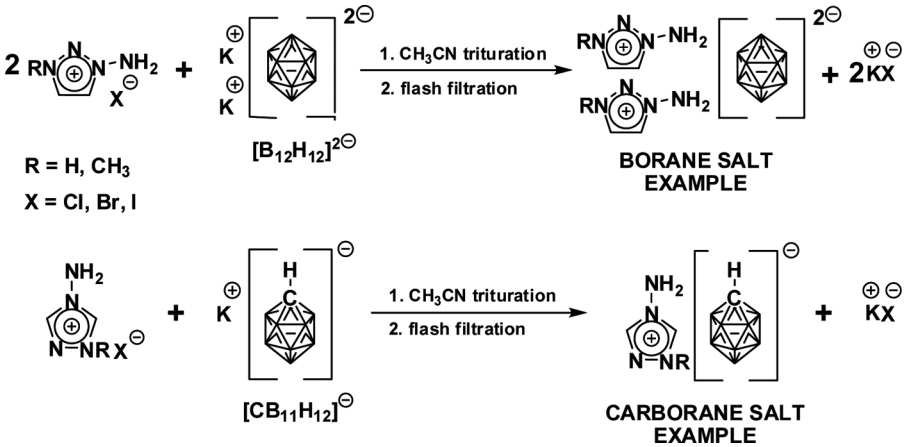
INTRODUCTION

In a previous publication,[1] a group of new water-insoluble binary heterocyclium (imidazolium and triazolium) *closo*-icosahedral borane $[B_{12}H_{12}]$ and carborane $[CB_{11}H_{12}]$ salts were synthesized with a one-step aqueous metathesis reaction in excellent yields. These unique salts were generated using an open-air benchtop procedure conducted by combining stoichiometric quantities of potassium borane or potassium carborane with a variety of heterocyclium chloride, bromide, or iodide salts. Mixing the two metathesis component salts in hot deionized (DI) water, followed by slow cooling in a refrigerator, produced these water-insoluble salt products and permitted trivial product isolation and efficient purification. These resulting binary heterocyclium borane and carborane salts were verified by NMR, infrared (IR), high-resolution m/z, and/or single-crystal x-ray analyses and were chemically free of any significant contamination by their associated by-product potassium halide precursor counterions. This latter issue was verified by direct ion chromatography analysis for the $[Cl]^-$ titer.

Other new binary heterocyclium (triazolium and tetrazolium) *closo*-icosahedral borane and carborane metathesis salts, however, possessed high solubility in water, and innovative alternative synthesis metathesis methodologies were needed for their preparation. These new synthetic procedures were developed as described in this article. Several other publications[2–4] also have been reported that used closed-system nonaqueous preparations of various binary solid salts containing only the *closo*-icosahedral carborane anion $[CB_{11}H_{12}]^-$ paired with a moderate selection of imidazolium cations and one pyridinium cation example.

RESULTS AND DISCUSSION

We sought a further generalization of this open-air aqueous benchtop metathesis methodology[1] for synthesizing water-soluble salts where additional triazolium cations and a new tetrazolium cation could be paired with the *closo*-borane and *closo*-carborane anions (Scheme 1). In pursuing this endeavor, at least two serious

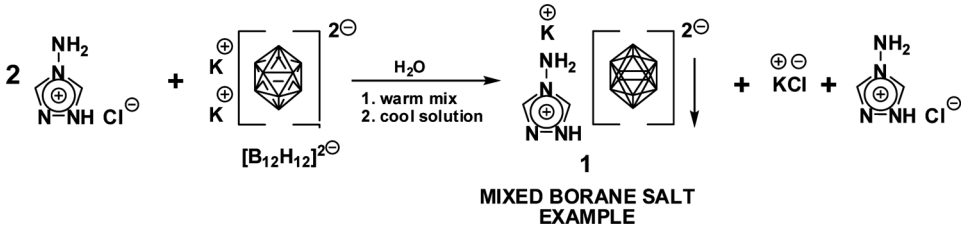


Scheme 1. Typical reactions of trituration-based metatheses.

complications had to be solved. First, when attempting to perform a simple metathesis by combining 2.0 equivalents of [4-amino-1-H-1,2,4-triazolium][Cl] with 1.0 equivalent of $K_2[B_{12}H_{12}]$ in warm DI water, instead of the desired adduct, a beautiful highly faceted crystalline solid deposited (Scheme 2), which consisted of the pure [4-amino-1-H-1,2,4-triazolium][K][$B_{12}H_{12}$] (**1**) salt product. The identity of this adduct was unambiguously ascertained by proton NMR integration and single-crystal x-ray crystallography (Fig. 1). This result likely occurred from a far lower solubility of the mixed mono-K/triazolium borane salt (**1**) compared to either of the starting materials or of the desired metathesis salt product (**2**) seen in Fig. 2. The mono-K salt (**1**) insolubility precluded a direct water-driven metathesis reaction and necessitated developing an alternative methodology. Second, expansion of aqueous metathesis combinations that pair these borane and carborane anions beyond previous imidazolium and triazolium examples[1] gave a variety of highly water-soluble salts. For example, the metathesis reaction of [5-amino-x-H-tetrazolium][Cl] with either the borane, $K_2[B_{12}H_{12}]$, or the carborane, $K[CB_{11}H_{12}]$, reactants yielded hydrated crystals of the desired product salts **4** and **5** as illustrated in Figs. 2 and 3, respectively. However, because of their high water solubilities, only very poor yields of the metathesis targets were recovered. Even highly concentrated aqueous solutions afforded poor product yields. Thus, direct water-driven metathesis reactions proved to be a highly inefficient process, especially given the expense of the commercial potassium borane or potassium carborane precursors. Development of an alternative nonaqueous methodology with a greater generality for water-soluble metathesis salt products became the important challenge addressed in this study.

Acetonitrile Trituration (Procedure A)

We investigated the combined use of exhaustive triturations with acetonitrile, followed by a flash filtration through silica gel (Scheme 1). This method exploited the significant solubility of many heterocylium borane and carborane salts in boiling anhydrous acetonitrile versus the relative insolubility of the corresponding KCl by-product. It also required determining the amount of KX by-product that a given dry volume of silica gel might have retained using a reasonable volume of eluting solvent. For KCl, 0.4473 g (6.0 mmol) was partially solubilized in 100 mL of warm acetonitrile. After cooling to room temperature, the resulting turbid liquid was passed through 40 mL (dry volume) of silica gel, overlaid with 20 mL (dry volume) of sea sand, and eluted with another 100 mL of acetonitrile. Less than 1 mg of KCl residue was collected after solvent removal.



Scheme 2. Formation of the mixed mono-K/triazolium borane salt.

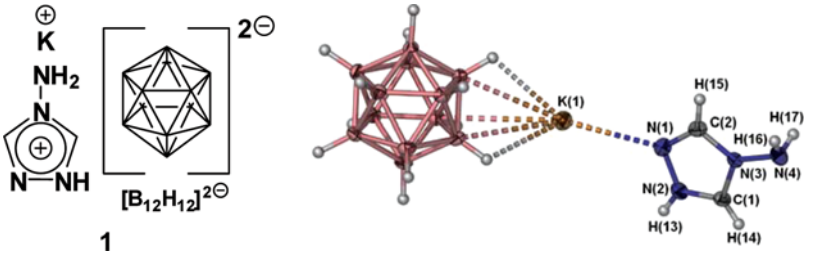


Figure 1. Graphical and molecular drawing of the mixed [4-amino-1,2,4-triazolium][potassium][$B_{12}H_{12}$] salt **1** with thermal ellipsoids shown at 50% probability level. (Figure is provided in color online.)

In this metathesis reaction process, once both solid salt reactants were mixed, our acetonitrile trituration/flash filtration approach was followed by careful removal of volatiles to give a series of finely divided amorphous powders. While many preliminary experiments were performed to seek a general recrystallization solvent mixture for these powders, and while some individual successes resulted, a general efficient solvent system for all salt product recrystallizations could not be found. So, rather than recrystallizing each individual adduct, spectroscopic examination of the amorphous solids was performed. This allowed a direct comparison for the effectiveness of the trituration/filtration procedures across a group of reactants. These isolated crude powders were indeed spectroscopically pure and had a moderately low content of $[Cl]^-$ (Table 1), in fair agreement with the blank experiments done on a bolus of KCl suspended in acetonitrile. While a couple of values were greater than expected (Table 1, salts **4** and **5**), varying the number of triturations, trituration volume, or a silica-gel-plug rechromatography might have reduced these halide concentrations. The $[Cl]^-$ measurement procedure used can be viewed in the Experimental section.

The use of exhaustive trituration/plug filtration worked for a considerable variety of heterocyclium halide starting materials. Replicate experiments with reactions involving 2–6 mmol of the starting heterocyclium halide were examined with no discernable variation in yield. For each preparative run, we performed a total of 10 separate triturations and then pooled the triturant samples in a flask, followed

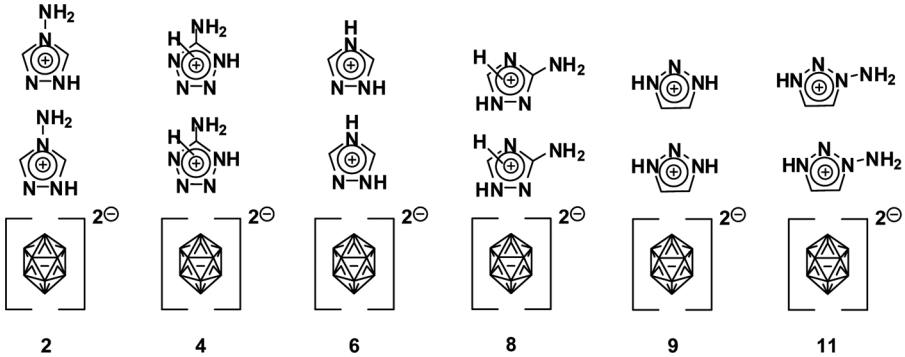


Figure 2. Synthesized binary heterocyclium borane salts.

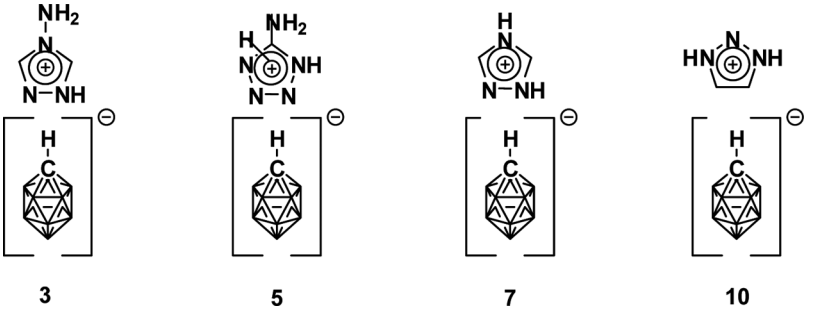


Figure 3. Synthesized binary heterocyclium carborane salts.

by cooling to room temperature prior to the flash filtration. For the trituration process to work at maximum efficiency and to minimize elution of the by-product KCl, using anhydrous acetonitrile was essential for successful flash filtration. High-performance liquid chromatography (HPLC)–grade acetonitrile from Aldrich conveniently was employed without any further purification by carefully wrapping the screw-cap-sealed bottle top with Parafilm after initially opening a new vessel. For this investigation, commercial silica gel of moderate sieve size (70–230 mesh; Merck) was optimal. Semiproportional scaling of the required silica gel from 22 mL (dry volume) to 40 mL (dry volume) and the additional eluting solvent volume from 80 mL to 120 mL were found to be satisfactory as the scale of reaction was increased from 2 to 6 mmol, respectively. After evaporation of the trace acetonitrile remaining in the stirbar/recovery flask apparatus, a proton NMR (dimethylsulfoxide, DMSO-d_6, solvent) performed on the residue indicated essentially complete removal of the starting metathesis reactant salts. When generalized to additional heterocyclium chloride examples beyond this article, such a trial NMR would indicate whether any further triturations were needed. This result could then be easily incorporated as feedback into a specific modified procedure. Heterocyclium iodides showed significant solubility in acetonitrile, so there could be instances where a greater amount of silica gel would be needed to remove all the KI. Our experimental efforts with heterocyclium iodides, however, focused on procedure B (discussed later) where silver nitrate was employed to drive an aqueous metathesis reaction to completion by silver halide by-product removal.

Eliminating the final traces of acetonitrile from the metathesis salt products initially proved to be difficult. The sluggishness in removal of the acetonitrile for

Table 1. Percentage of residual chloride ion content in synthesized salts **2–11**

	Compound									
Parameter	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Chloride by weight (%)	0.47	0.19	3.06	2.41	0.45	0.71	<udl[a]	0.30	<udl[a]	0.06
Detection limit (%)	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.02

[a]Below detection limit.

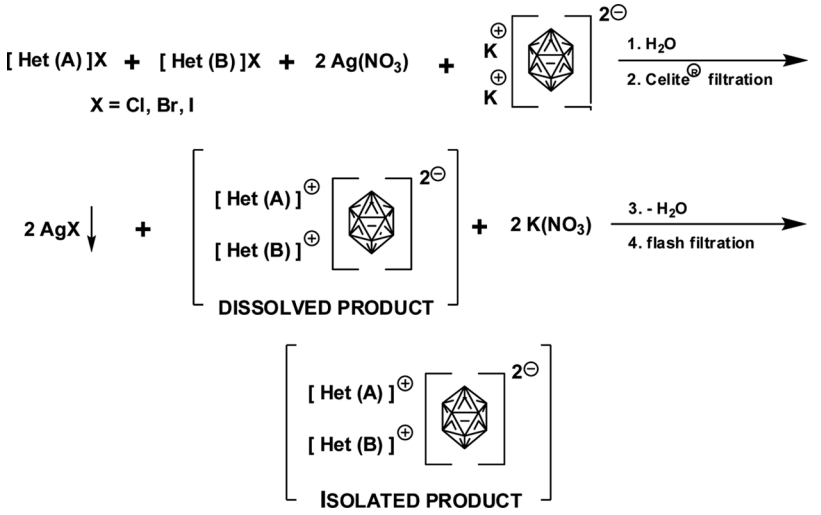
many examples of borane and carborane salts suggested some sort of significant borane-based solvent interaction. A simple azeotrope-type process was developed where a few milliliters of deionized water were added to the sample followed by removal of all volatiles at high vacuum (final P ~ 40–50 mTorr). Occasional modest heating of the flask with a heat gun, while under vacuum azeotrope conditions and after water addition, was repeated three times. This process effectively removed all the residual acetonitrile. Incorporating this final solvent "distillation" into the overall process gave isolated yields of spectroscopically pure anhydrous metathesis product salts (**2**–**11**) as finely divided amorphous solids in overall yields that ranged from 85% to 98% (Figs. 2 and 3). For completeness, moderately water-insoluble examples from our earlier publication,[1] [4-amino-1-H-1,2,4-triazolium][*closo*-$CB_{11}H_{12}$] (**3**) and [1-amino-3-H-1,2,3-triazolium]$_2$[*closo*-$B_{12}H_{12}$] (**11**), were examined by procedure A. The isolated flash-filtered products were obtained in good yields and with spectroscopic data identical to those previously reported.[1]

There was no significant difference in the results whether one employed either the potassium borane or potassium carborane as starting materials for this acetonitrile trituration metathesis procedure. The starting boron-containing materials were purchased from Katchem in the Czech Republic and used without any further purification.[1]

Silver-Ion-Driven Metathesis (Procedure B)

A second method for driving the metatheses reactions to completion used a stoichiometric amount of aqueous silver nitrate to precipitate the halide gegenions as AgX. This process produced several useful advantages and one possible disadvantage. The procedure was particularly valuable in driving this metathesis reaction to completion by the extreme insolubility of the AgX by-product. Furthermore, as was previously suggested for borane salts,[1] this process conveniently permitted the first intentional example for synthesizing potential "ternary"* mixed diheterocyclium borane salts, where two different singly charged heterocyclium cations were paired with the one borane dianion (Scheme 3). This was possible by reacting 1 mol each of two different heterocyclium halides with 1 mol of the potassium borane and using 2 equivalents of silver nitrate in water solvent to yield mixed dication heterocyclium borane salts like **12–14** seen in Fig. 4. The immediate silver halide precipitate was filtered through a bed of moist Celite, affording a colorless aqueous filtrate that contained the desired product salt as well as 2 equivalents of KNO_3. Removal of the water via a high vacuum line gave a fluffy white powder. Dissolution of a small sample in DMSO-d_6 afforded a crude proton NMR spectrum that conformed

*The term *binary* fits the carborane salts that stoichiometrically contain one heterocyclium cation paired with the carborane anion. For discussions in this report and others,[1,6] the term *binary* also is extended to the borane salts that contain the *same* two heterocyclium cations paired with the borane dianion. The term *ternary* is reserved for the mixed borane salts where two *different* heterocyclium cations are stoichiometrically paired in a 1:1 ratio with the borane dianion. Similarly, salt **12** with a heterocyclium $[Het]^+$ cation and potassium $[K]^+$ cation stoichiometrically paired with the *same* borane dianion is considered to be a *ternary* salt.



Scheme 3. Silver-ion-driven metathesis and mixed borane salt capability.

exactly to the expected relative correct integrations of *all* key peaks.† The initial mass balance was near theory when the presence of 2 equivalents of KNO_3 were included. Upon filtration of a resuspension of the crude solid in acetonitrile through a plug of silica gel, overlaid by sand, followed by removal of all volatiles (again using the thrice "water azeotrope treatment"), an amorphous white solid was isolated that generally conformed to the expected proton and carbon NMR. To ensure the KNO_3 by-product was removed on the silica-gel plug, a blank run using 0.6066 g (6.0 mmol) of KNO_3 was partially solubilized in 100 mL of warm acetonitrile. After cooling to room temperature, the resulting suspension was passed through 40 mL (dry volume) of silica gel, overlaid with 20 mL (dry volume) of sea sand, and eluted further with 100 mL of acetonitrile. Solvent removal afforded less than 1 mg of recovered residue.

In experiments to synthesize a mixed heterocyclium borane salt (**12**) containing two different mono-cations (Fig. 4), we initially were highly gratified that, after the plug filtration, this approach indeed gave the two heterocyclium cations in a precise 1:1 ratio based on proton NMR integrations of their distinctive peaks. However, when comparing the integration of the very sharp N-methyl singlets (3H) to the borane B-H multiplet (12H), the borane integration was always slightly (ca. 5%) higher than expected. Similar results appeared for the other mixed heterocyclium boranes (**15** and **16**) displayed in Fig. 4. We were not certain what caused this slight

†The synthetic method used, the significantly greater than 50% yields, and the proton NMR integrations are consistent with the formation of mixed salts **12–14**. However, it is possible the same result would be observed if the isolated solids contained either an exact one-third mixture of the two pure salts and the mixed salt or of some mixture containing an equal percentage of the two pure salts with the mixed salt constituting the remaining 100% sample. In any case, two different heterocyclic mono-cations are in some arrangement of intimate contact with one borane dianion, which provided at least one interesting property, eutectic melting-point depression. Recrystallization of ternary salts **12–14** was not attempted because of a concern that a cation redistribution might result.

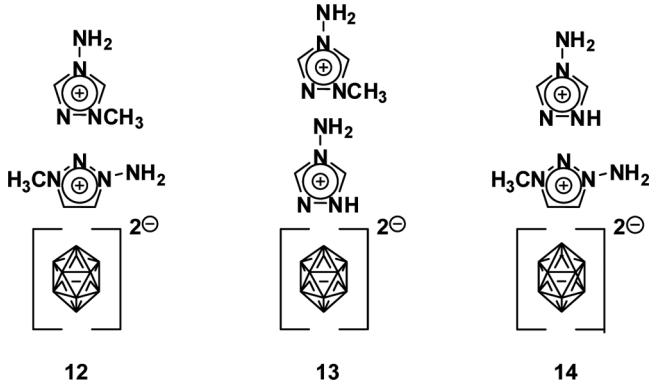


Figure 4. Synthesized mixed diheterocyclium borane salts.

anomaly but hypothesized that it probably resulted from overloading the adsorbent active sites on the silica gel with both the metathesis components as well as with the KNO_3 by-product. Attempts to modify the elution by taking smaller numbers of column volumes of elutant basically lowered the overall yield, but this anomalous shortfall in the ratio of heterocyclium peak integrations versus the borane dianion B-H integration was not improved. Nevertheless, within the caveat of the 5% integration anomaly, moderately pure crude solids of various mixed dication heterocyclium salts with the desired borane dianion were obtained. These results simply are noted and accepted as an inherent limitation of procedure B.

The possible synthesis of ternary mixed diheterocyclium borane salts, which pair two different singly charged heterocyclium cations with the borane dianion (Fig. 4), raised an interesting question regarding eutectic melting-point behavior. While it is well known that a physical admixture of two neutral compounds often affords eutectic behavior, resulting in a lower melting point, a recent literature article revealed similar behavior with heterocyclium salts.[5] When three solid salts were physically mixed in equimolar ratios, the admixture gave a lower intersalt eutectic melting point that resulted in a room-temperature melt. This led to the supposition that a ternary mixed diheterocyclium borane salt, such as **12** with its two dissimilar heterocyclium cations, might provide a lower melting point via an intrasalt eutectic behavior than the melting points exhibited by the two related binary salts **15**[1] and **16**.[1] Binary salts **15** and **16** each paired two identical heterocyclium cations with a borane dianion, where the two cations of one salt (*e.g.*, **15** or **16**) were the same as one each of the two dissimilar dications in the mixed diheterocyclium borane salt (**12**). A melting-point depression would also be expected, relative to each pure salt, when the two individual binary salts, **15** and **16**, were physically mixed via an intersalt eutectic behavior.[5] Thus, similar intrasalt (**12**) and intersalt (**15** and **16**) melting-point behaviors might be expected, and indeed, this was the case.

Preparation of the ternary mixed diheterocyclium borane salt (**12**) by the silver nitrate process (procedure B) afforded a white solid with a crude, unrecrystallized mp of 136–142 °C. Any attempt at recrystallizing the 1:1 mixture of cations in **12** could have afford an enrichment in one or the other of the heterocyclium cations. The flash filtration, by virtue of eluting the two cations and the dianion in electrostatic

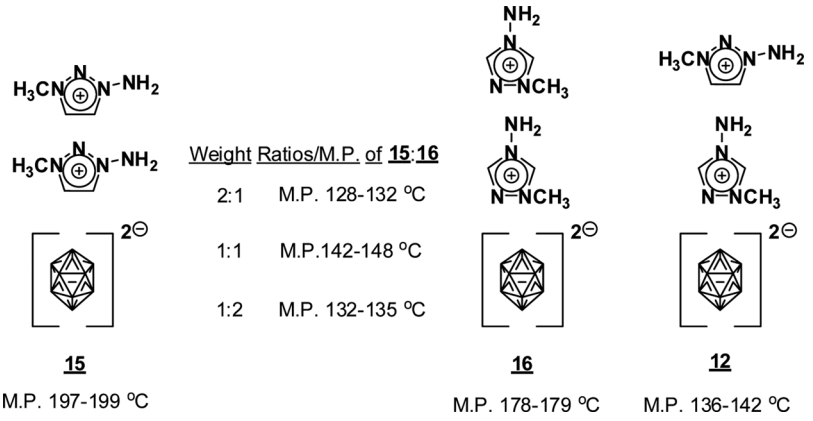


Figure 5. Comparison of intersalt and intrasalt melting-point depressions.

neutrality, preserves the 1:1 ratio to within experimental error of the proton NMR integration. When the two recrystallized individual binary salts having mp of 197–199 °C for **15** and 178–179 °C for **16** were physically mixed in a 1:1 ratio by weight, a mp of 142–148 °C was obtained for this admixture (Fig. 5). Subsequent improved melting points of pure salts **15** and **16** were obtained from that originally determined for Ref. 1. For completeness, a 2:1 ratio physical admixture of salts **15** and **16** gave a mp of 128–132 °C, and a 1:2 ratio displayed a mp of 132–135 °C. Thus, either a physical mixture of individual binary heterocyclium salts **15** and **16**, or a synthesized ternary mixed diheterocyclium borane salt (**12**), respectively, provided a similar intersalt or intrasalt eutectic melting-point lowering (Fig. 5).

EXPERIMENTAL

Caution! While no special precautions were taken in synthesizing and handling these borane-based salts, they were shown to be high-energy materials and could be thermally,[6] impact, friction, and/or spark (ESD) initiated to rapid energy-releasing phenomena. Hazards testing was conducted on salts **2**, **4**, **5**, and **11**. Impact initiation testing determined the 100% value where no initiation occurs, and salt **11** was the most sensitive at 84 Kg-cm, while salt **5** was the least sensitive at 250 Kg-cm. For comparison, the following more sensitive impact Kg-cm values where 50% sample initiation results for known explosives were CL-20 at 33, PETN at 67, HMX at 115, and RDX at 117. Salt **2** was most sensitive to friction initiation at 14.4 Kg-cm, while salts **4** and **5** were the least friction sensitive at 21.6 Kg-cm. Salt **2** also was the most sensitive to spark initiation (ESD test) at 0.0025 J, and salt **5** was the least ESD sensitive at 1.00 J.

All neutral heterocycles that were converted to the hydrochloride (aqueous concentrated HCl followed by recrystallization from $EtOH/Et_2O$) or to the methiodide (CH_3I followed by recrystallization from $EtOH/Et_2O$) were purchased commercially with one exception. The 1-amino-1,2,3-triazole was synthesized as described in the literature.[7] DI water was obtained from an in-house Millipore MILL-Q reagent-grade water system at an 18-megaohm-cm purity level. All organic solvents were

commercially purchased and were either reagent grade or HPLC purity. Most important, the acetonitrile used in the triturations and flash filtrations was HPLC grade, and the solvent container was carefully re-Parafilmed after each use to minimize any accumulated moisture.

A Brüker Avance 400 digital NMR instrument was used to obtain both proton (^{1}H) and carbon (^{13}C) spectra. Because this project is primarily one involving process chemistry, we used commercial samples of Katchem $K_2[B_{12}H_{12}]$ that contained a small amount of $[NHEt_3]_2[B_{12}H_{12}]$ salt as an impurity. By direct proton integration against the main component, this impurity was approximately 1.5%. One component of this impurity peak overlapped with the B-H multiplet, but this integration contribution was negated (by simple subtraction) from the (B-H) integrations for each new metathesized salt. However, this $[NHEt_3]_2[B_{12}H_{12}]$ "impurity" provided a constant marker for our reaction mixtures because the product salts were not recrystallized. The sole exception to this for the salts (**1–14**) was (**1**) which, when recrystallized in water solvent, was completely devoid of the $[NHEt_3]_2[B_{12}H_{12}]$ impurity.

Fourier transform–infrared spectra (FTIR) were taken on powdered samples using a Nicolet 6700 spectrometer in air with a horizontal attenuated total reflectance (HATR) optical system.

Commercial Opti-Melt apparatus was used with video playback software. For typical acetonitrile-trituration runs, the isolated amorphous solids were not subjected to melting-point determination.

The $[Cl]^-$ ion concentration was determined by ion chromatography using a Waters HPLC equipped with a Waters 432 conductivity detector and a Phenomenex Star-Ion A300 100×4.3 mm ID (PEEK) column. A borate/gluconate eluent was used, and system conditions were set according to Waters method 980895. Each salt sample was weighed between 0.01 mg to 0.05 mg in a plastic class B centrifuge tube and diluted to 25 mL using type I ultrapure water. Samples that did not readily dissolve were heated to 80 °C with a plastic centrifuge cap. Each sample was passed through an IC Millex LG 0.2-μm syringe filter prior to injection. A three-point calibration curve was generated using blank, 1-ppm, and 10-ppm NIST traceable chloride standard. Concentrations were determined by comparing peak area response of the samples to the standard calibration curve.

Procedure A Synthesis: General Procedure

After weighing out the corresponding stoichiometric quantities of the heterocyclium halide salt and the appropriate potassium carborane or potassium borane salt, the solids were placed in a recovery flask equipped with a stirbar (flask and stirbar are tarred together) and a Vigreaux reflux tube. Addition of pure acetonitrile (HPLC grade only) was followed by placing the apparatus in a hot oil bath (internal T = 161–165 °C). After the contents of the flask reached a vigorous reflux, the suspension was then cooled to near room temperature, and the supernatant was carefully transferred to an Erlenmeyer flask. Exhaustive trituration was repeated 10 times, using an empirically derived volume of acetonitrile (10 mL for a 6-mmol scale and 6 mL for a 2 to 3-mmol scale of carborane or borane), and resulted in complete removal of the reactive species while most of the by-product potassium halide remained in the original recovery flask. After cooling to room temperature, the

combined trituration solutions in the Erlenmeyer flask were poured over an acetonitrile-moistened bed of 35 mL (dry volume) of silica gel and 8 mL (dry volume) of washed sea sand packed in a 125-mL coarse frit glass filter. An additional 100 mL of acetonitrile was passed through the adsorbent bed. The combined solvent was then rotovapped to dryness. To remove the last traces of acetonitrile, addition of 2 mL of DI water was followed by pumping at high vacuum, with periodic heat gun treatment, thereby affording a solid residue. This "semi-azeotrope" treatment was repeated a total of three times. This afforded a clean white amorphous powder whose proton NMR integration was excellent, whose [halide] weight percentage was generally small (Table 1), and whose yields were acceptable. Individual samples were not recrystallized because each product required considerable experimentation to find a suitable single or mixed optimal solvent combination for recrystallization.

Procedure B Synthesis

This procedure has been adapted for a mixed cation system and was based on the reaction used to prepare the mixed diheterocyclium borane, [4-amino-1-Me-1,2,4-triazolium][1-amino-3-Me-1,2,3-triazolium][*closo*-$B_{12}H_{12}$] (**12**). The crystalline iodide [4-amino-1-Me-1,2,4-triazolium][I] (0.6781 g; 3.00 mmol), the crystalline iodide [1-amino-3-Me-1,2,3-triazolium][I] (0.6781 g; 3.00 mmol), the borane $K_2[B_{12}H_{12}]$ (0.6601 g; 3.00 mmol), and the silver nitrate (1.0192 g; 6.00 mmol) were carefully weighed out separately, and each was transferred separately to four different 50-mL beakers. To each of the beakers were added 4 mL of DI water, and the contents were warmed on a hot plate. Slowly, in the previous order, the contents of the first three beakers were transferred to the fourth beaker, and each of the first three beakers was rinsed with 2.0 mL of DI water. The resulting combined grayish suspension was stirred with a glass rod and then filtered through a pre-prepared moist bed of Celite. The beakers were rinsed with a final 5 mL of DI water. The filtrate was placed in a tared recovery flask and pumped for 40 h on a high vacuum line (final $P \sim 35$ mTorr). The contents of the recovery flask were swirled with 70 mL of hot anhydrous acetonitrile, cooled to RT, and poured through a 125 mL (coarse frit) glass funnel with a pre-equilibrated (acetonitrile) bed of silica gel (38 mL dry volume) and overlain with sea sand (10 mL dry volume). Elution with a total of 200 mL of anhydrous acetonitrile was followed by removal of solvent (rotovapped and high vacuum line). To the crude residue was added 3 mL of DI water, and the contents were heated repeatedly with a heat gun, while the volatiles were slowly removed under high vacuum. This process was repeated a total of three times to afford an off-white amorphous solid (0.9253 g of spectroscopically pure residue. See this ternary salt (**12**) below for spectroscopic details.

Selected Data

[4-Amino-1-H-1,2,4-triazolium][K][*closo*-$B_{12}H_{12}$] (1). From 2.410 g (20.0 mmol) of [4-amino-1-H-1,2,4-triazolium][Cl] and 2.2003 g (10.0 mmol) of $K_2[B_{12}H_{12}]$ in 11.0 mL DI water held at reflux for 10 min and cooled to 4 °C overnight, there was isolated 1.3754 g (51.7%) of massive distorted rhombs [mp 207.2 °C (softening), 252.3–254.9 °C liquification with rapid gas evolution]. This product was

subjected to single-crystal x-ray crystallography. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 9.47 (s, 2H), ~8.6 (br exchangeable peak 3H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 144.03. FTIR (HATR method; significant peaks) 3318, 3226, 3145, 3109, 3061, 3036, 2479, 2461, 2435, 1747, 1733, 1623, 1546, 1524, 1425, 1360, 1334, 1202, 1070, 1034, 979, 946, 880 cm^{-1}.

[4-Amino-1-H-1,2,4-triazolium]$_2$[*closo*-$B_{12}H_{12}$] (2). Yields: proc. A = 85.8%; proc. B = 91.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 9.43 (s, 4H), ~7.95 (br exchangeable peak, 6H), 1.9–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 144.05. FTIR (HATR method; significant peaks) 3322, 3305, 3224, 3113, 2464, 2439, 1622, 1552, 1520, 1422, 1356, 1328, 1302, 1205, 1152, 1062, 1029, 976, 939, 870, 711, 682, 612, 576 cm^{-1}.

[4-Amino-1-H-1,2,4-triazolium][*closo*-$CB_{11}H_{12}$] (3)[1]. Yield: proc. A = 93.7%. ^{1}H NMR (400.132 MHz, DMSO-d_6 (center peak = 2.50) δ 9.49 (s, 2H), ~7.95 (br exchangeable peak, 3H), 2.38 (br s, 1H), 2.3–0.7 (complex multiplet, 11H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 144.03, 50.75. FTIR (HATR method; significant peaks) 3612, 3346, 3285, 3126, 3052, 3023, 3003, 2929, 2514, 1634, 1610, 1512, 1422, 1352, 1319, 1201, 1144, 1094, 1062, 1025, 939, 919, 874, 711, 612 cm^{-1}.

[5-Amino-x-H-Tetrazolium]$_2$[*closo*-$B_{12}H_{12}$] (4). Yields: proc. A = 98.4%; proc. B = 96.5%). ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ ~ 8.16 (br exchangeable peak, 8H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 156.22. FTIR (HATR method; significant peaks) 3559, 3497, 3403, 3330, 3199, 2480, 1699, 1634, 1581, 1442, 1409, 1311, 1258, 1140, 1066, 1046, 1001, 911, 774, 735, 715, 682, 625 cm^{-1}.

[5-Amino-x-H-Tetrazolium][*closo*-$CB_{11}H_{12}$] (5). Yields: proc. A = 94.3%; proc. B = 96.8%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ ~ 7.13 (br exchangeable peak, 4H), 2.38 (br s, 1H), 2.2–0.6 complex multiplet, 11H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 155.89, 50.73. FTIR (HATR method; significant peaks) 3608, 3534, 3444, 3346, 3318, 3056, 2533, 1708, 1642, 1605, 1450, 1438, 1381, 1278, 1127, 1091, 1058, 1029, 760, 715, 666, 592, 559 cm^{-1}.

[1-H-4-H-1,2,4-Triazolium]$_2$[*closo*-$B_{12}H_{12}$] (6). Yield: proc. A = 94.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ ~ 13.19 (br exchangeable peak, 4H), 9.22 (s, 4H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 143.54. FTIR (HATR method; significant peaks) 3438, 3297, 3278, 3252, 3225, 3126, 3058, 3020, 2461, 1644, 1557, 1523, 1398, 1264, 1143, 1063, 1033, 949, 877, 714, 653 cm^{-1}.

[1-H-4-H-1,2,4-Triazolium][*closo*-$CB_{11}H_{12}$] (7). Yield: proc. A = 94.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ ~ 12.52 (br exchangeable peak, 2H), 9.23 (s, 2H), 2.37 (br s, 1H), 2.3–0.7 (complex multiplet, 11H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 144.06, 50.72. FTIR (HATR method; significant peaks) 3469, 3367, 3281, 3130, 3028, 2517, 1740, 1556, 1520, 1418, 1352, 1172, 1152, 1086, 1025, 886, 866, 711, 620 cm^{-1}.

[3-Amino-1-H-x-H-1,2,4-triazolium]$_2$[*closo*-$B_{12}H_{12}$] (8). Yield: proc. A = 90.1%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ ~ 13.37 (br exchangeable peak, 4H), 8.30 (s, 2H), ~7.99 (br exchangeable peak, 4H), 1.8–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 150.90, 139.48. FTIR (HATR method; significant peaks) 3379, 3309, 3260, 3183, 3154, 3113, 2464, 1695, 1610, 1593, 1573, 1389, 1340, 1258, 1066, 1033, 952, 866, 715, 645, 604, 564 cm^{-1}.

[1-H-3-H-1,2,3-Triazolium]$_2$[*closo*-$B_{12}H_{12}$] (9). Yield: proc. A = 90.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 13.26 (br s, 4H), 7.96 (s, 4H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 130.35. FTIR (HATR method; significant peaks) 3220, 3154, 3134, 3060, 3044, 2999, 2460, 1560, 1454, 1409, 1368, 1287, 1242, 1127, 1074, 968, 833, 776, 764, 715, 670 cm[1].

[1-H-3-H-1,2,3-Triazolium][*closo*-$CB_{11}H_{12}$] (10). Yield: proc. A = 96.2%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 12.44 (br s, 2H), 7.96 (s, 2H), 2.38 (br s, 1H), 2.3–0.7 (complex multiplet, 11H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 130.30, 50.79. FTIR (HATR method; significant peaks) 3604, 3362, 3240, 3158, 3136, 3051, 3001, 2951, 2905, 2516, 1946, 1854, 1657, 1611, 1553, 1503, 1453, 1407, 1357, 1230, 1118, 1091, 1068, 1022, 960, 883, 795, 760, 710, 671, 621 cm^{-1}.

[1-Amino-3-H-1,2,3-triazolium]$_2$[*closo*-$B_{12}H_{12}$] (11)[1]. Yield: proc. A = 96.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 8.41 (extremely br s, 6H), 7.942 (d, J = 0.8 Hz, 2H), 7.715 (d, J = 0.8 Hz, 2H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 132.10, 124.19. FTIR (HATR method; significant peaks) 3301, 3224, 3187, 3154, 3126, 2484, 2451, 1593, 1544, 1466, 1401, 1295, 1168, 1148, 1107, 1074, 1058, 1021, 992, 944, 886, 792, 727, 656 cm^{-1}.

[4-Amino-1-Me-1,2,4-triazolium][1-amino-3-Me-1,2,3-triazolium][*closo*-$B_{12}H_{12}$] (12). Yield: proc. B = 90.8%. ^{1}H NMR (400.132 MHz, DMSO-d_6 (center peak = 2.50) δ 10.04 (s, 1H), 9.15 (s, 1H), 8.730 (d, *J* = 1.2 Hz, 1H), 8.597 (d, *J* = 1.2 Hz, 1H), 8.25 (s, 2H), 6.92 (s, 2H), 4.22 (s, 3H), 4.03 (s, 3H), 1.7–0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d_6 center peak = 39.51) δ 145.02, 142.91, 131.51, 126.85, partially resolved N-CH_3 peaks on the DMSO-d_6 carbon heptet 39.75 vs. 39.71 and 38.92 vs. 38.88. FTIR (HATR method; significant peaks) 3628, 3555, 3326, 3301, 3248, 3220, 3117, 3097, 3076, 2464, 2018, 1765, 1712, 1638, 1605, 1573, 1532, 1479, 1434, 1401, 1381, 1315, 1209, 1172, 1062, 960, 866, 796, 715, 657, 608 cm^{-1}.

[4-Amino-1-Me-1,2,4-triazolium][4-amino-1-H-1,2,4-triazolium][*closo*-$B_{12}H_{12}$] (13). Yield: proc. B = 81.2%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 10.04 (s, 1H), 9.44 (s, 2H), two overlapping singlets with essentially the same chemical shift), 9.14 (s, 1H), 7.00 (extremely br s, 5H), 4.03 (s, 3H), 1.8–0.0 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 145.06, 144.05, 142.95, and 38.97. FTIR (HATR method; significant peaks) 3739, 3583, 3563, 3542, 3506, 3318, 3228, 3109, 3064, 3036, 2942, 2901, 2476,

1748, 1732, 1618, 1556, 1520, 1425, 1324, 1262, 1205, 1168, 1058, 1033, 980, 939, 886, 866, 754, 711, 678, 653, 612, 555 cm^{-1}.

[4-Amino-1-H-1,2,4-triazolium][1-Amino-3-Me-1,2,3-triazolium][*closo*-$B_{12}H_{12}$] (14). Yield: proc. B = 71.7%. ^{1}H NMR [400.132 MHz, DMSO-d_6 (center peak = 2.50)] δ 9.44 (s, 2H), 8.728 (d, $J = 1.2$ Hz, 1H), 8.595 (s, $J = 1.2$ Hz, 1 H), 8.20 (extremely broad s, 5H), 4.22 (s, 3H), 1.7–0.1 (complex multiplet, 12H). ^{13}C NMR [100.624 MHz, DMSO-d_6 (center peak = 39.51)] δ 144.04, 131.53, 126.87 (N-Me peak not resolvable within the DMSO-d6 heptet). FTIR (HATR method; significant peaks) 3546, 3318, 3224, 3109, 3032, 2460, 1748, 1732, 1622, 1564, 1524, 1475, 1434, 1401, 1364, 1324, 1238, 1209, 1062, 1038, 980, 948, 907, 874, 809, 715, 682, 618 cm^{-1}.

Crystal Data for $C_2H_{17}B_{12}KN_4$ (1)

$M_r = 266.02$, orthorhombic, space group *Pna2*(1), $a = 12.166(2)$, $b = 11.443(2)$, $c = 9.868(2)$ Å, α, β, $\gamma = 90°$, $V = 1373.6(4)$ $Å^3$, F-(000) = 544, $\rho_{calcd} = 1.286$ gcm^{-3}, $Z = 4$, $\mu = 0.361$ mm^{-1}, crystal size $0.3 \times 0.2 \times 0.2$ mm^3, θ range 2.44 to 28.34, index ranges $-16 \le h \le 16$, $-15 \le k \le 15$, $-13 \le l \le 13$, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 296(2)$ K, 296. The single-crystal x-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a Smart Apex 2 detector with the χ axis fixed at 54.74° and using MoK_α radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1–4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs. Measured data 29305 of which 3418 ($R_{int} = 0.0231$) were unique. Transmission factors min/max 0.641/0.746, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0231$, $wR2 = 0.0624$, R indices (all data): $R1 = 0.0246$, $wR2 = 0.0613$, GOF on $F^2 = 1.052$. CCDC-787684 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data+request/cif.

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REFERENCES

1. Shackelford, S. A.; Belletire, J. L.; Boatz, J. A.; Schneider, S.; Wheaton, A. K.; Wight, B. A.; Hudgens, L. M.; Ammon, H. L.; Strauss, S. H. Pairing heterocyclic cations with *closo*-icosahedral borane and carborane anions, I: Benchtop aqueous synthesis of binary triazolium and imidazolium salts with limited water solubility. *Org. Lett.* **2009**, *11*, 2623–2626.
2. Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. Designing ionic liquids: Imidazolium melts with carborane anions. *J. Am. Chem. Soc.* **2000**, *122*, 7264–7272.

3. Zhu, Y.; Ching, C.; Carpenter, K.; Xu, R.; Selvaratnam, S.; Hosmane, N. S.; Maguire, J. A. Synthesis of the novel ionic liquid [N-pentylpyridinium][*closo*-$CB_{11}H_{11}$]. *Appl. Organometal. Chem.* **2003**, *17*, 346–350.
4. Nieuwenhuyzen, M.; Seddon, K. R.; Teixidor, F.; Puga, A. V. Ionic liquids containing cluster anions. *Inorg. Chem.* **2009**, *48*, 889–901.
5. Bai, Y.; Cao, Y.; Zhang, J.; Wang, M.; Li, R.; Wang, P.; Zakeeruddin, S. M.; Grtzel, M. High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nat. Mater.* **2008**, *7*, 626–630.
6. Shackelford, S. A.; Belletire, J. L. Heterocyclic salt synthesis and rational properties tailoring. *Centr. Europ. J. Energ. Mater.* **2009**, *6*, 219–237.
7. Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. Synthesis, characterization, and structural investigations of 1-amino-3-substituted-1,2,3-triazoliium salts, and a new route to 1-substituted-1,2,3-triazoles. *J. Heterocycl. Chem.* **2005**, *42*, 19–27.